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SEASONAL VARIATION IN SOUTHERN PINE TERPENES

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ABSTRACT

Monoterpene and volatile organic compound (VOC) concentrations measured at some mills have large swings of a seemingly seasonal nature and a great amount of variability is evident. The question to be resolved is whether these differences are attributable to wood handling and mill operations or to biological factors associated with tree growth. Information in the available literature primarily describes monoterpene production and release associated with foliage, not wood. This paper describes the results of a study comparing the amounts of VOCs released from drying southern pine wood to the amount of monoterpenes collected from loblolly pine (*Pinus taeda*) increment cores. Handling and storage have been shown to potentially affect quantitative results, but it appears that more monoterpenes are produced in trees in response to higher temperatures and increased precipitation. At least for reasonably fresh material, measurements of monoterpenes and VOC concentrations at mills probably reflect climatically-affected patterns of tree development.

INTRODUCTION

In 1995 a southern pine oriented strand board (OSB) mill reported wide variability in Method 25A VOC emissions measured at flake drying operations in the field. Measurements could not be reproduced even when taken on the same day, and the mill was interested in alternative means of making measurements; consequently, samples of fresh flakes were sent to the Institute of Paper Science and Technology for analysis on a more-or-less monthly basis beginning in February 1995. These samples were wrapped, stored cold, and dried in a 130°C tube furnace equipped to monitor total hydrocarbon emissions (1). It was anticipated that there would be some variability among the monthly samples due to different proportions of heartwood and sapwood, and that additional variability might result from handling, storage conditions, or convenience sampling at the mill. Nonetheless, the results of laboratory analyses from the first two years' samples were surprising in that the VOC concentrations of individual samples varied by as much as 500% (from ~ 300 :g/g to 1500 :g/g on a wet basis) (Figure 1).

Consistent with the mill's previous Method 25A measurements and, as expected, due to the samples' origins, significant variability was apparent even within single sampling dates. It appeared probable that more VOCs were collected during the warm months during this sampling period; it also appeared that there might be some interactive effect of ambient temperature and rainfall as wet weather often coincided with warm weather (Figure 2), but (at least in part because of the data variability) it was not clear whether this hypothesis was provable or even if these data were typical. The company requested further work, including measurements of monoterpenes from standing trees, to verify the scatter (and possible trends) in the flake VOC measurements and to determine, if possible, the reasons for the large variation in the measured VOC concentrations. This work is still in progress, but this report provides the information currently available.

LITERATURE REVIEW

As part of this investigation, the available literature was surveyed to determine if variability in total VOC (monoterpene) content had been studied before. No information was found that described a seasonal variation of monoterpenes in the trunks of standing trees, although one study reported differences in the turpentine content of southern pine chips going into a kraft paper mill over a two-year period (7). The analyzed chips had about 30% higher turpentine contents in cool months than in the summer months; this appears to contradict the initial analytical results of the OSB flakes, but the report provided no information about handling or sampling of the chips. An investigation of *Pinus elliottii* by Bin *et al.* (2) found that the amount of "turpentine" steam-distilled from the resin of tapped trees increased from July to November, and that the major constituents were ∀-pinene and ∃-pinene. ∀-Pinene constituted about two-thirds of this mixture, although the proportion of ∃-pinene was somewhat greater during the cooler months. A number of reports describe the seasonal changes in monoterpenes of needles, twigs or seedlings for various species, but most of these studies were conducted over periods of one year or less. For example, Lerdau and Dilts (5) found "seasonal declines" in monoterpene concentration but constant emissions from foliage;

Lerdau *et al.* (6) later reported a strong effect of temperature and seasonality on emissions. Fulton *et al.* (3) reported that the volatile emissions from black spruce trees increased with temperature. He-Ping (4) reported that the relative contents of some volatile terpene compounds collected from the foliage of *Pinus tabulaeformis* varied between the summer and the winter months; for example, the α-pinene and β-pinene concentrations both increased by about 25% during the summer months compared to the January samples. Others have also reported that the proportions of the various monoterpenes have seasonal changes (10). There are evidently important physiological and/or genetic aspects of terpene biosynthesis that affect tree-to-tree variations. Raffa (9) has also reported that the monoterpene concentration in grand fir (*Abies grandis*) increased nearly four-fold after insect attack. None of this information directly answered the immediate questions, but the indications of possible seasonal effects on terpene expression were intriguing.

EXPERIMENTAL

An experiment was planned that would enable comparisons between the VOC emissions from fresh southern pine OSB flakes and the monoterpene contents of samples obtained from standing southern pine trees. In a continuation of the initial study, samples of southern pine flakes were requested on a periodic basis from the North Carolina OSB mill for laboratory VOC analysis and plans were made to monitor the monoterpene concentrations in a longitudinal study using twelve straight, well-formed loblolly pine (*Pinus taeda*) trees (each approximately 39 cm (15 inches) in diameter and forty years old) in the Mississippi State University's John W. Starr Memorial Forest. These trees were naturally reseeded - not from a plantation - and all of the trees should have a somewhat similar genetic provenance because they were located in the same area. From March to September 1997, one 0.5 cm (0.2 inch) diameter increment core was taken from each tree per month for analysis of the monoterpene and resin acid content. The first core from each tree was taken at breast height, and successive cores were offset by several inches both horizontally and vertically/upwards (Figure 3). To prevent infection, each hole was plugged with a maple dowel immediately after the core was taken. Each core was divided into three portions prior to analysis (inner third, center third, and outer third) to enable the study of intra-tree monoterpene distributions at a later date. The specimens were stored in methylene chloride and sonicated, and the extract was analyzed with a gas chromatograph to determine the amount of monoterpenes present; appropriate internal standards were used, but no claims are made that the data are quantitatively accurate. The increment core segments were dried in an oven overnight at 103°C to obtain their dry weight, and a weighted average concentration for the entire core was calculated based upon the differently sized areas of the tree cross-section represented by each one-third of the increment core.

In September of 1997 the sample trees (although clearly marked) were cut by an overzealous logging equipment demonstrator, and after a one-month hiatus the experiment was continued with another twelve trees in a nearby location. These trees are of similar age and size to the original sample trees. Like the original sample, the second group was naturally reseeded and was not part of a plantation planting. One of the twelve trees was cut and dissected during the month of December 1998, to determine whether the repeated sampling and plugging caused injury-induced resin to bleed internally and bias the data, but no evidence was seen to indicate that this was anything but an occasional problem.

Figure 4 shows the monoterpene concentration data collected and analyzed through December 1998; a locally-weighted (loess) regression line (span = 0.5) has been drawn through the data to illustrate the overall trend in the face of such evident variability. Figure 4 shows that there are slight differences from one year to the next (no doubt partly caused by sampling different trees), but most of the change in concentration appears to be due to season or some associated climatological component. During this sampling period the loblolly pine trees had a greater monoterpene content during the cooler and wetter months of the year, but there was uncertainty whether this was a typical response as Mississippi weather was slightly cooler and significantly wetter than usual during this experiment due to the prevailing El Niño weather pattern. There is a wide range in the monoterpene values determined; considering all the data, there is about a 700% difference between the highest and the lowest analyzed values caused by both variability within the 12-tree sample and variability due to seasonal influences.

The Mississippi data (analyzed on an oven-dry wood basis) were compared with the Institute of Paper Science and Technology data for the North Carolina OSB flakes (analyzed on a green weight basis). Figure 5 shows two loess regression lines (span = 0.5) based on averaged data for each sampling date; considering the differences in both analytical techniques and in the geographical origins of the specimens, the Figure 5 curves are remarkably similar. As both North Carolina and Mississippi experience similar weather, these data would appear to indicate that the analyses of the OSB flakes were either unaffected by sampling, handling and storage, or that these influences were insufficient to mask the trends of monoterpene expression in standing trees.

In contrast to the monoterpene variations seen during the joint North Carolina – Mississippi sampling period (March 1997 through December 1998), Figure 1 showed that monoterpenes apparently peaked in North Carolina during the warmer months of 1995 and 1996. To resolve this apparent incongruity, all four years' data from the North Carolina portion of the study were plotted (Figure 6) and compared to seasonal data obtained from the Climvis data set from the National Oceanic and Atmospheric Administration (NOAA) (8) (Figures 7 – 8). Between February 1995 and April 1999 the North Carolina data showed four peaks, and although the first two were similar, the third was lower and seemed to peak at a different time of the year (cool months instead of warm months) (Figure 7). During the period from March 1997 through July 1998 the weather in the southeastern United States was affected by an El Niño weather pattern (slightly cooler average temperatures with 20 cm or more precipitation than usual compared to "normal" climate conditions for the same time period), so the precipitation data were also compared to the VOC data (Figure 8). Figure 9 shows the VOC trend together with the data for temperature and precipitation.

It appears that the VOCs from the OSB flakes were maximized during periods which had both warm temperatures and high rainfall. VOCs seemed to be at their minimal levels during periods that had both low temperatures and low rainfalls, and VOCs arose to intermediate levels during the cool months of 1997-1998 when rainfall significantly exceeded normal levels. It was also interesting to note that the VOCs apparently rose in early 1996 in response to temperature as the rainfall lagged temperature somewhat that year. A rigorous statistical analysis of these data is just beginning, but it seems likely that VOC levels in southern pine trees are positively affected by both temperature and rainfall and that higher levels of both are required for the maximum monoterpenes to be expressed in standing trees. This analysis is consistent with the observations taken in Mississippi for the more limited timeframe which included the El Niño season.

The potential for handling and storage conditions to affect VOC measurements was addressed in a series of controlled experiments. Southern pine chips from freshly-cut 16- to 18-year-old trees were taken directly from a paper mill chipper and samples of these chips were analyzed immediately (using five replications) for both α-pinene and β-pinene (which together comprise most of the monoterpenes in loblolly pine). Additional samples, sterilized using sodium azide and maintained at room temperature, were measured every two or three days for two weeks. Approximately one-third of the α-pinene was lost during the first week, after which no further losses were noted. β-pinene concentrations did not appear to be affected. Based on these results it is concluded that the handling and storage history of the flakes sent from the mill might affect the monoterpene concentrations of some samples and that this may have affected the variability inherent in the data presented here.

SIGNIFICANCE OF FINDINGS

There was a great deal of variability from sample to sample during this analysis period, and this variability may be affected by handling or sampling considerations. In the trees sampled, however, the typical monoterpene concentrations varied by as much as 300 to 500% during the course of a year (depending on whether averaged data or data trends are chosen for comparisons). Between the lowest and the highest monoterpene concentrations recorded to date in the longitudinal study of standing trees there is a difference of more than 700% over time, and there is no reason to believe that the variability might be less for trees sampled from other locations. The Mississippi and North Carolina data patterns are similar, suggesting that the data presented here are indicative of real trends and that they are not artifacts of analytical techniques. Seasonal influences appear to affect the monoterpene concentration in the stemwood of these loblolly pines, and it seems likely that there is an interactive effect of temperature and rainfall. A more rigorous statistical study of the effects of temperature and precipitation on monoterpenes/VOCs is underway. Overall, it seems likely that a significant part of the variability in OSB flake dryer emissions and kraft mill terpene recoveries can be traced to climatically-affected physiological effects, and the rest can be attributed to handling and other factors.

Acknowledgements
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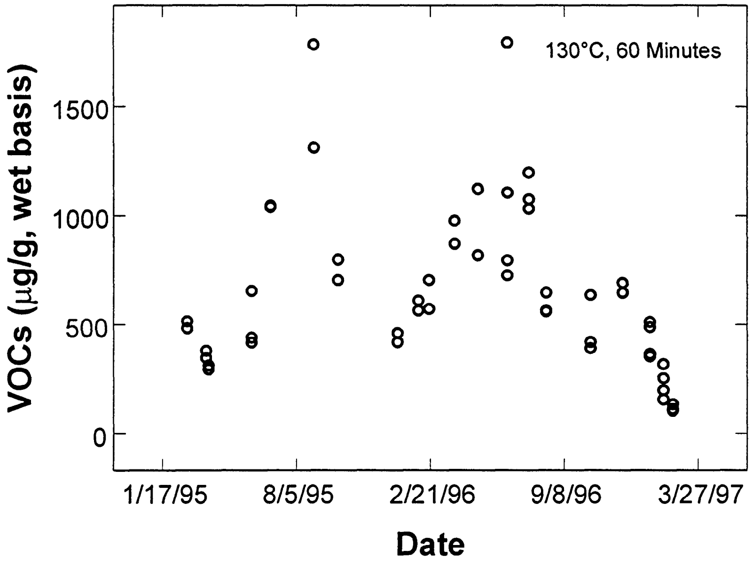

Figure 1: Results of laboratory analyses of southern pine flakes from a North Carolina OSB mill, 2/95–2/97.

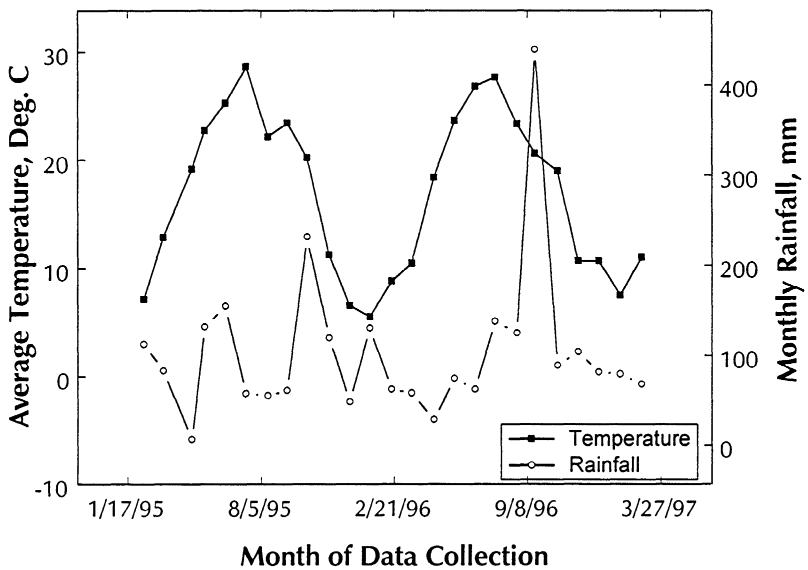

Figure 2: Rainfall and temperature data corresponding to North Carolina OSB mill location.

Figure 3: One of the sampled trees with two increment-cored locations marked.

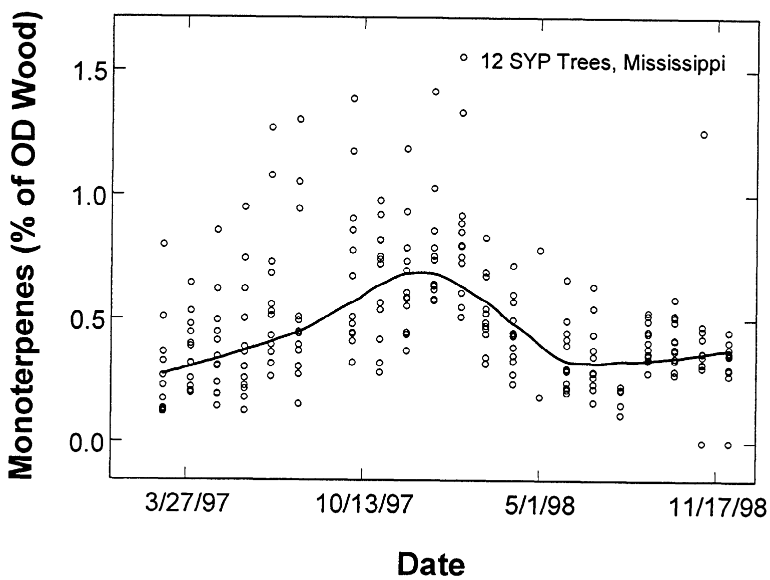

Figure 4: Total monoterpenes as a percent of ovendry (OD) wood from the longitudinal study of 12 loblolly pine trees in Starkville, Mississippi (loess regression line shown overlaid on data, degree = 2, span = 0.5).

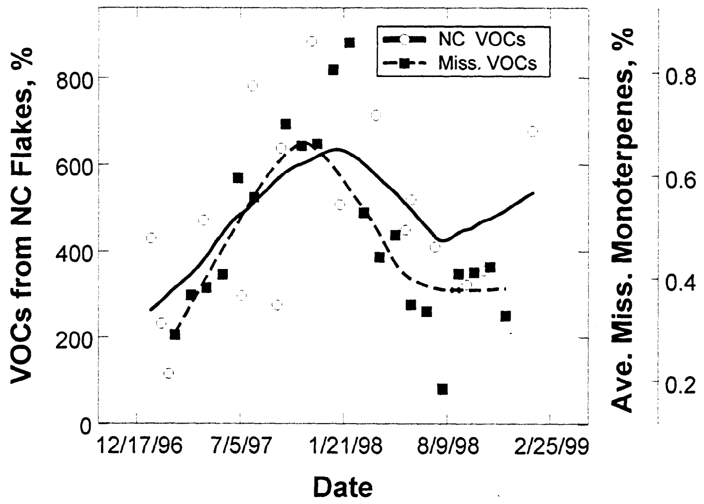

Figure 5: Comparison of the amounts of monoterpenes from Mississippi tree analyses with VOCs from North Carolina OSB flakes.

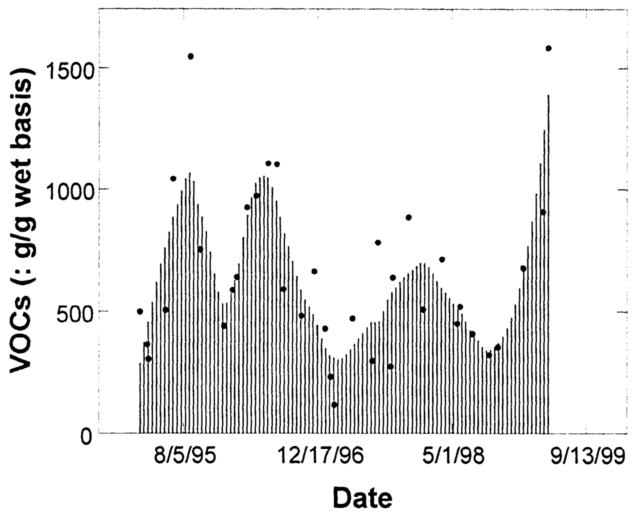

Figure 6: North Carolina data for VOCs from February 1995 through April 1999. Loess regression shown for data.

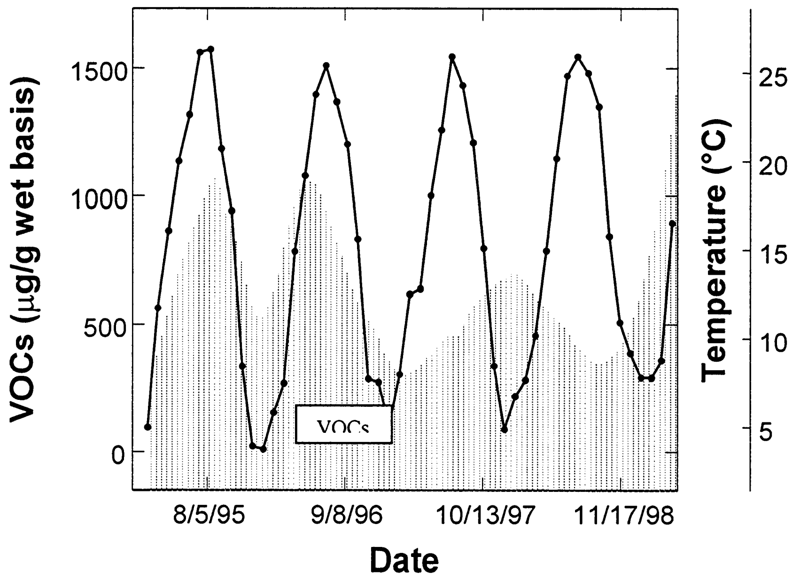

Figure 7: North Carolina VOC data and temperature data from Raleigh, NC.

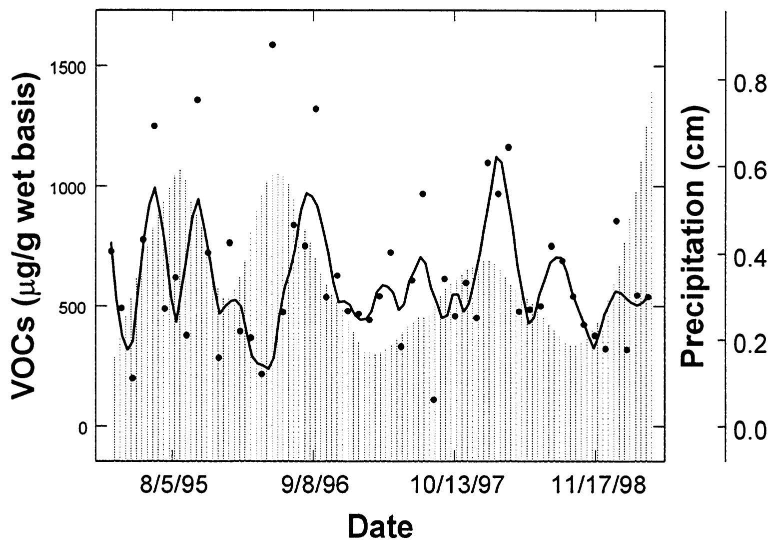

Figure 8: VOCs and precipitation data with trend line for North Carolina during sampling period 1995 – 1999.

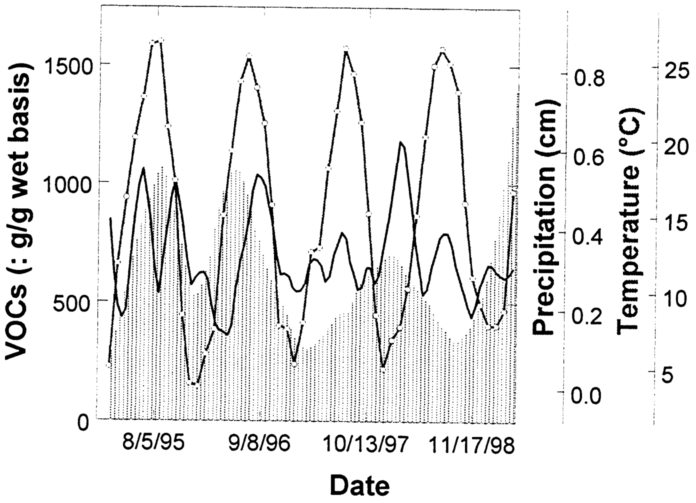

Figure 9: VOCs, precipitation and temperature in North Carolina during sampling period 1995–1999.